

*Bel. to corresp. to IR 1,452,218*  
**PATENT SPECIFICATION**

NO DRAWINGS

Inventors: GHEORGHE DAN SUCIU, RODICA BUHESCU and GABRIELA  
POPESCU-BRADET

L118.146



L118.146

Date of Application and filing Complete Specification: 9 July, 1965.

No. 29141/65.

Complete Specification Published: 26 June, 1968.

© Crown Copyright 1968.

Index at acceptance: —C3 R(3D14A, 3D20, 3D27, 3N1, 3N7, 3P1, 3P5, 3P6)

Int. Cl.: —C 08 g 17/08

### COMPLETE SPECIFICATION

### Process for Producing Polycarbonates by Interfacial Polycondensation

- I HORATIU IANCU, Deputy Minister of Ministerul Industriei Petrolului si Chimiei, a Rumanian Ministry, of str. Scaune, nr.1, Bucharest, Rumania, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a process for producing polycarbonates, by interfacial polycondensation.
- 15 The interfacial polycondensation process is frequently used in the preparation of some polyesters from acid dichlorides and dihydroxylic compounds. According to said process, polycarbonates are obtained on an industrial scale from phosgene and aromatic dihydroxylic compounds.
- 20 The discontinuous phosgenation in the system formed by the aqueous alkaline solution of the dihydroxylic compound and the organic solvent is the method generally used for obtaining polycarbonates.
- 25 In this system phosgene is added whilst stirring the alkaline solution and organic solvent; after the phosgenation, the reaction mixture is further stirred for the completion of the polycondensation. The polymer solution thus obtained is then purified in known manner.
- 30 For the adjustment of the molecular weight of polycarbonate previously established quantities of catalysts (e.g. tertiary amines or quaternary ammonium salts) and chain terminating agents (e.g. monofunctional phenols) may be introduced into the reaction mixture before or after the phosgenation.
- 35 In the known continuous processes, the polycarbonate synthesis is carried out in packed reaction columns, (British Specification 1,008,584), screw-conveyor type reactors, kettle type reactors in series, tubular flow reactors, (British Specification 923,192) etc. The reaction proceeds at the organic-water interface which is more less continuous (in the former two cases) or discontinuous (drops), in the latter two cases.
- 45 Disadvantages of the known continuous processes consist in the relatively low reactor productivity obtained due to the restricted interfacial area and also to the difficulties in removing efficiently the reaction heat.
- 50 In another process (British Specification No. 1,026,514) a "pre-formed" reaction medium is obtained during a discontinuous step after which the process is carried out continuously with or without previously emulsifying the "pre-formed reaction medium".
- 55 The processes according to which one works at elevated temperatures have the disadvantage that the phosgene and alkali consumptions are increased since the undesired secondary reactions between the active acidic groups and NaOH have a reaction rate which rises more rapidly with rising temperature than does the polycondensation reaction rate.
- 60 In a further known continuous system, there is claimed in British Patent Specification No. 923,192 a process for the production of high-molecular weight, linear polycarbonates with improved mechanical properties, wherein the known reaction of organic dihydroxy compounds with phosgene and/or bischlorocarbonic acid esters of organic dihydroxy compounds in the presence of organic monohydroxy compounds, acid-binding agents, tertiary amine or quaternary ammonium compounds and inert solvents which dissolve polycarbonates is carried out continuously.
- 65 70 75 80
- [Price 4s. 6d.]

The present invention has for its object the elimination or mitigation of the disadvantages of the known processes.

Accordingly, the present invention is a continuous process for the production of polycarbonates, wherein the known interfacial polycondensation of a dihydroxylic compound and phosgene, in the presence of a suitable catalyst and a chain terminating agent and an inert organic solvent, is carried out in a reactor into which the aqueous and organic liquid phases containing the reactants are continuously introduced, and into which said aqueous and organic liquid phases immediately on reaching the reactor are emulsified by intimate mixing, and the emulsion containing the reaction product is continuously withdrawn from said reactor.

The reaction may be carried out for example in a single reactor or in two reactors, while in the latter case phosgene and the dihydroxy compound catalyst, chain terminating agent and solvent may be introduced either in the first reactor, or in both reactors, in suitable proportions. It is convenient that the reactor or reactors be operated completely filled with reaction mixture. Thus the relative position of the reactors is immaterial. These two reactors may constitute a single unit from a construction point of view, that is they may be two compartments within a common casing.

For polycarbonate synthesis according to the method of the present invention, the necessary dwell time based on the effluent volume, does not exceed 20 seconds when working with a single reactor. This short reaction time arises from the emulsification of the reaction components and so a good contact between the phases and reactants is possible. The reactor may be very compact since no heat transfer problems need arise, as in a preferred feature of the process the reactants and solvent are pre-cooled, preferably below 0°C, before admission to the reactor.

Any suitable inert organic solvent may be used, but a preferred solvent is methylene dichloride. An example of a suitable dihydroxylic compound is diphenylol propane (i.e. 2,2 - (4,4 - dihydroxydiphenyl) - propane). The molecular weights of the polyesters, especially of the polycarbonates produced, can be adjusted according to requirements by the known methods by means of catalysts and the chain terminating agents.

The molecular weight distribution produced compares favourably with that obtained in a discontinuous system.

When it is desired to produce polyesters with a special low content of low-molecular-weight fractions (in the case of polycarbonates, to produce a polymer with a low content of fractions with molecular weights below 5000—10,000) it is advantageous to operate in a two reactor system. The catalyst and the

chain terminating agent may be continuously fed, together with the effluent from the first reactor, into the second reactor.

In order to allow close control of the molecular weights and to reduce the quantity of the COCl terminal groups of the polyester chain, the catalyst and the chain terminating agent may be divided between the first and second reactor.

The mixing in the reactors must produce emulsification of the reactants, and may be performed either by using conventional high efficiency stirrers or by any other devices capable of producing the desired emulsification, for example by ultrasonic methods. Purification of the obtained polyester may be performed by using any of the suitable known methods.

The following examples illustrate, but in no way limit, the application of the present invention to the synthesis of polycarbonates.

#### EXAMPLE 1

Into a reaction vessel of capacity 200 ml provided with vigorous stirring means, an aqueous alkaline solution of diphenylolpropane (containing 6% NaOH and having a molar ratio of diphenylolpropane to NaOH of 1:2.6) and methylene chloride, are continuously introduced by means of metering pumps with approximately equal volumetric flow-rates (of about 18 l/h each). A continuous stream of phosgene having a flow-rate (about 0.96 kg/h) is also admitted to the vessel such that the chlorine ion concentration in the aqueous phase of the effluent from the vessel is about 1.2 mols/litre. The aqueous alkaline solution admitted to the vessel contains also  $3.1 \times 10^{-3}$  mole triethyl-amine (catalyst) and  $2.2 \times 10^{-3}$  mole phenol (chain terminating agent) per mole of diphenylolpropane.

Prior to entering the reactor, the aqueous phase and the methylene chloride are separately pre-cooled to about -2.5°C.

The stirring is sufficiently vigorous that the organic phase and aqueous phase are immediately emulsified within the reaction vessel.

The temperature in the reactor does not rise above 28°C. In the reactor the phosgene is completely consumed. The dwell time of the combined liquid phases is 18 seconds. Emulsified reaction mixture is continuously withdrawn from the reactor and is neutralized, and the aqueous and organic phases thus resulting are separated; the latter is then submitted to purification according to known methods. The molecular weight of the polycarbonate obtained is 25,000—30,000.

#### EXAMPLE 2

The operating conditions as regards reactants and solvent concentrations, flow rates and temperatures and stirring are the same

as in Example 1. The reactor is fed with a phosgene solution in methylene chloride obtained by feeding the phosgene into the methylene chloride stream before the latter is cooled to  $-2.5^{\circ}\text{C}$ . The concentrations of the triethyl amine and the phenol in the aqueous phase are  $3.1 \times 10^{-3}$  and  $1.9 \times 10^{-3}$  mole per mole of diphenylol propane, respectively.

The effluent from the reactor is processed as in Example 1. The molecular weight of the polycarbonate thus obtained is 35,000—40,000

### EXAMPLE 3

Into a reaction vessel of capacity 200 ml. provided with vigorous stirring means, an aqueous alkaline solution of diphenylol propane (containing 6% NaOH and having a molar ratio of diphenylol propane to NaOH of 1:2.4) and methylene chloride are continuously introduced by means of metering pumps with volumetric flow-rates in the approximate ratio of 3 to 2 (i.e. 18 l/h and 12 l/h respectively). A continuous flow of phosgene is also admitted to the vessel, having a flow rate such that the chlorine ion concentration in the aqueous phase of the effluent from the reactor is about 1.4 moles/l. Prior to entering the reactor the aqueous phase and the methylene chloride are separately pre-cooled to  $-3.5^{\circ}\text{C}$ . The stirring is sufficiently vigorous to emulsify the contents of the reaction vessel.

The temperature in the reactor does not exceed  $29^{\circ}\text{C}$ . The dwell time of the combined liquid phases in the reactor is 19.1 sec.

The effluent of this reactor passes into a second reaction vessel which consists of a compartmented column of capacity 1500 ml provided with powerful stirring means in every compartment and into which concurrently with the effluent from the first reactor is introduced an aqueous 15% NaOH solution whose flow rate is such that in the outlet solution from the column the concentration of NaOH is not less than 0.15 mols/litre.

Together with the effluent from the first reactor, there is introduced into the column a stream of methylene chloride with the same volumetric flow rate as that introduced into the first reactor and which has such a concentration of triethylamine and phenol that the delivered amount of these corresponds respectively to  $4 \times 10^{-3}$  and  $2 \times 10^{-3}$  moles per mole of diphenylol propane originally introduced into the first reactor in the aqueous alkaline solution. In the column the dwell time of the reaction mixture is 400 sec. The temperature in the column does not exceed that of the first reactor, though no cooling is necessary.

The product discharged from the column is neutralized (i.e. by aid of  $\text{CO}_2$ ) upon which separation of organic and aqueous liquid

phases occurs; the organic phase is then submitted to purification by known methods. The obtained polycarbonate has a molecular weight of 55,000—60,000.

### EXAMPLE 4

The working conditions are the same as in Example 3. In order to decrease further the low molecular weight fractions of the final product, in the first reactor a stream of triethylamine dissolved in the methylene chloride is introduced. The flow of triethylamine corresponds to  $2 \times 10^{-3}$  moles per mole of diphenylol propane fed. The flow rate of triethylamine and phenol fed into the column correspond to  $3 \times 10^{-3}$  and  $2.2 \times 10^{-3}$  moles per mole of diphenylol propane respectively. All other conditions being the same, the polycarbonate obtained has a molecular weight of 60,000—65,000. The amount of polymer having a molecular weight under 15,000 (obtained upon fractionation) is 5—6% i.e. about half of that obtained in Example 3.

The process according to the invention has the following advantages:

High reactor productivity is obtained by virtue of the improved mass transfer across the liquid-liquid interface due to the emulsification of the aqueous and organic phases.

As the reactor or reactors may be operated completely filled, the reaction space may be used to the maximum. Space is also saved if two reactors are used as they may form a unit from a construction point of view. This unit is not cumbersome since it can work in any convenient position, i.e. vertical, horizontal or intermediate.

The problem of removing the reaction heat is eliminated by pre-cooling the raw-materials and the solvent.

Due to the low working temperature the amounts of reactants consumed by side reactions (neutralisation of the  $-\text{COCl}$  by NaOH) is much reduced.

The process is very flexible and enables a wide range of molecular weights and a reduction of the molecular weight distribution of the product to be obtained.

### WHAT I CLAIM IS:—

1. A continuous process for the production of polycarbonates, wherein the known interfacial polycondensation of a dihydroxylic compound, and phosgene, in the presence of a suitable catalyst and a chain terminating agent and an inert organic solvent is carried out in a reactor into which the aqueous and organic liquid phases containing the reactants are continuously introduced, and into which said aqueous and organic liquid phases immediately on reaching the reactor are emulsified by intimate mixing, and the emulsion containing the reaction products is continuously withdrawn from said reactor.

2. A process according to claim 1 wherein

the desired temperature in the reactor is maintained solely by pre-cooling the reactants and the solvent.

3. A process according to claim 1 or 2  
5 wherein the reaction is completed in a second reactor, to which a catalyst and a chain terminating agent are continuously added and in which vigorous stirring is maintained.

4. A process according to claim 3 wherein  
10 additional quantities of reactants and/or solvent are introduced into the second reactor.

5. A process according to claim 3 or 4 wherein both the catalyst and chain terminating agent are continuously introduced in suit-

able proportions both into the first and into  
the second reactor. 15

6. A process for producing polyesters substantially as hereinbefore described with reference to any of the Examples.

7. Polycarbonates, whenever produced by  
the process according to any of the preceding  
claims. 20

H. D. FITZPATRICK & CO.,  
Chartered Patent Agents,  
5 Park Gardens, Glasgow, C.3.  
and  
27 Chancery Lane, London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.  
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.